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Influence of temperature and frequency on the electrical parameters of a polycrystalline silver thallium selenide AgTlSe

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Abstract : The a.c electrical properties of bulk AgTlSe have been studied in the frequency range 10^2 - 10^5 Hz and in the temperature range 300 - 495 K. Measurements revealed that the a.c conductivity $\sigma(\omega)$ varied as ω^s, where the index s was variable and always less than unity. The temperature dependence of both a.c. conductivity and the index s is reasonably well interpreted by the correlated barrier hopping (CBH) model. Measurements of capacitance and loss tangent showed a well defined decrease with increasing frequency and an increase with increasing temperature. An interpretation is presented, based on existing theory, for the case of a thermally activated process when using ohmic contacts

Keywords : Electrical properties, silver thallium selenide

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1. Introduction

The chalcopyrite semiconductors are ternary compounds of great interest to scientists and engineers, because they show promising applications in the area of visible and infrared LEDs, infrared detectors, optical parametric oscillators, up converters and solar cells [1- 5]. The addition of Tl in the binary system Ag-Se is expected to affect some of its physical properties [6]. Thallium – containing chalcogenide have attracted much attention because of their technological application to acousto-optical devices [6, 7]. Most of the work in the fields of amorphous and crystalline semiconductors have been done on thin films and conclusions drawn from such studies may not necessarily be applicable to bulk materials. Very little information is available in the literature on conduction phenomena in bulk crystalline AgTlSe . Therefore, the present communication reports some new results on electrical properties over a wide range of temperatures and frequencies for bulk Ag Tl Se. These measurements provide useful information about the conduction mechanism in bulk Ag Tl Se .

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2. Experimental work

The bulk AgTlSe was prepared in the conventional way [8, 9] by melting the mixture of five nine purity (99.999%) elements mixed in exact stoichiometric proportions in sealed evacuated (about 10^{-5} Torr) ampoule held at 1170 K for several hours, shaken a number of times to ensure thorough mixing , and then slowly cooled at room temperature over two days . The resulting samples were cut with a wire cutting machine and finally they were lapped and mirror polished.

X - Ray diffraction characterization of powder Ag Tl Se was carried out using filtered CuK_{α} radiation (Philips X' Pert) operated at 40 kV and 25mA . The result of the X - ray diffraction patterns obtained for AgTlSe in powder form, illustrates that the bulk sample has polycrystalline nature as shown in Figure 1. Results of careful analysis with J.C.P.D.S. card no.(35-1140) indicate an orthorhombic structure of Ag Tl Se.

The chemical composition of the bulk sample was monitored by carrying out quantitative analysis energy - dispersive spectroscopy, (EDX) on a Joel 5400 scanning electron

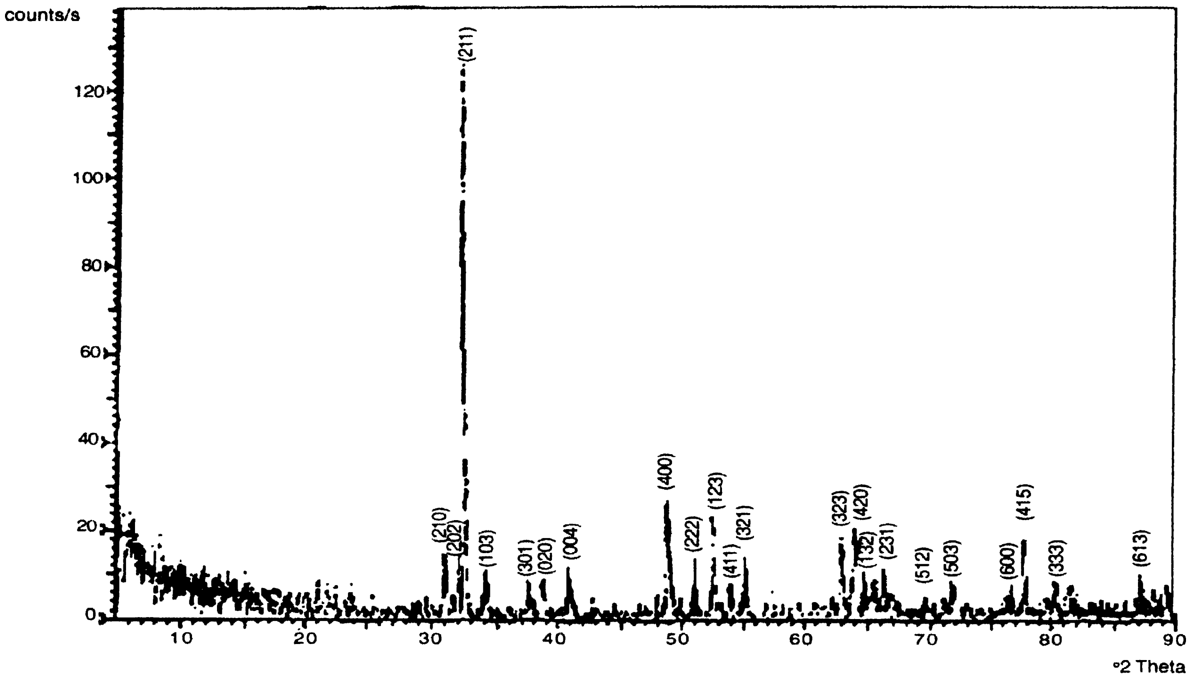

Figure 1. X-ray diffraction patterns of bulk AgTlSe.

microscope. These measurements were used to obtain the correct composition (AgTl Se).

For a.c. measurements, the bulk sample of Ag Tl Se was sandwiched between two ohmic Al electrodes as lower and upper electrodes. A programmable automatic RLC bridge (PM 6304 Philips) was used to measure the impedance Z, the capacitance C and the loss tangent tan δ directly. The sample was placed in a holder specially designed to minimize stray capacitance. Temperature of the sample was measured using a chromel – alumel thermocouple .

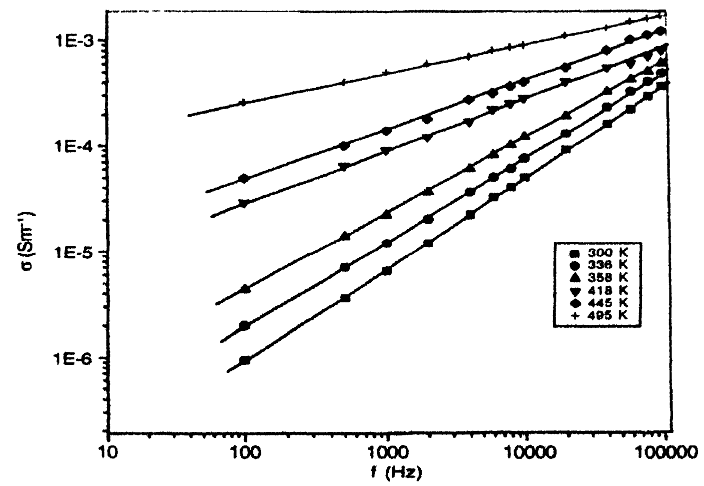

Figure 2. Dependence of a.c. conductivity on frequency at different fixed temperatures.

3. Results

The variation of a.c. conductivity with frequency at differen fixed temperatures (300 - 495K) is shown in Figure 2. It is clea from the figure that the conductivity increases linearly wit frequency.

Figure 3 represents the thermal variation of th frequency exponents determined over the frequency rang The values of s were derived from slopes of these lines of th figure. It is clear from this figure that s decreases with increasin temperature.

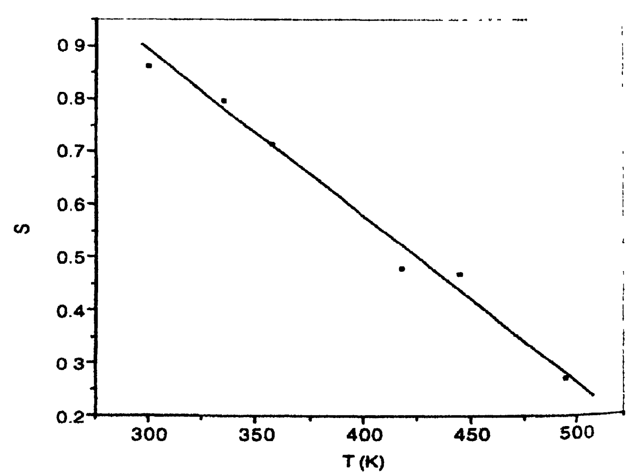

Figure 3. Dependence of the exponent s on temperatures for the frequency range.

The variation in the a.c. conductivity with inverse temperature at six different frequencies is presented in Figure 4. It is clear from the figure that a.c. conductivity decreases linearly with the inverse temperature.

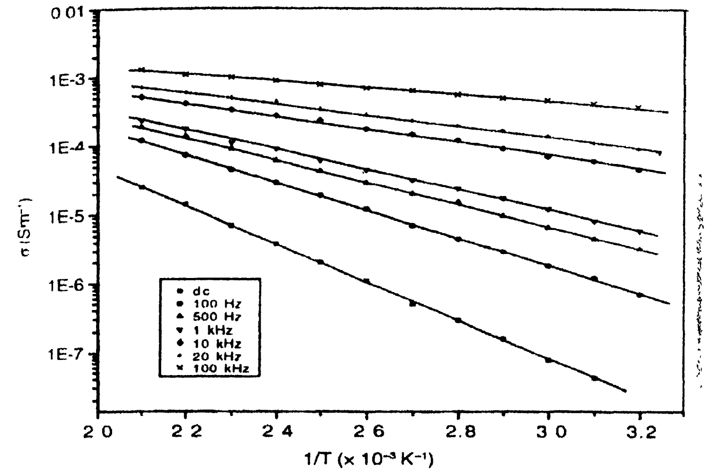

Figure 4. Dependence of a.c. conductivity on inverse temperature at different frequencies.

The activation energy of conduction ΔE_σ is calculated at different frequencies from the slopes of lines of Figure 4. The frequency dependence of the activation energy for the investigated bulk AgTlSe is shown in Figure 5. The obtained a.c. activation energy at any frequency is much lower than the d.c. activation energy obtained (0.57± 0.02 eV) over the same range of temperature. It can also be seen that ΔE_σ tends to decrease with increasing temperature.

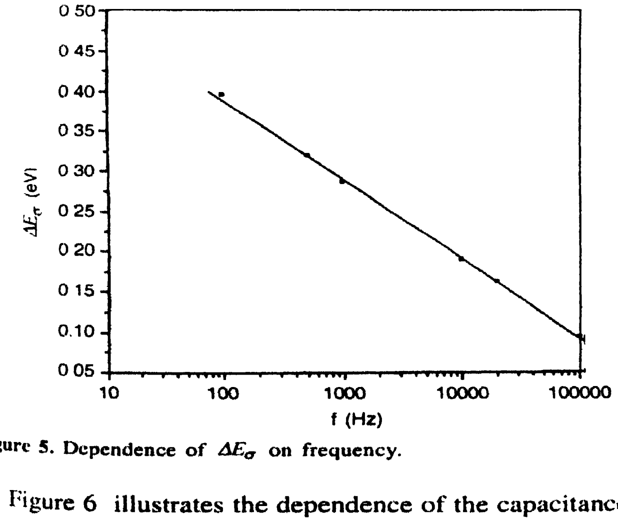

Figure 5. Dependence of ΔE_σ on frequency.

Figure 6 illustrates the dependence of the capacitance on temperature at various fixed frequencies (100Hz - 100kHz). At temperatures below about 336 K, the capacitance is independent of temperature but above 336 K, it becomes temperature-dependent with the appearance of separate curves characteristic of frequency. These results are plotted in Figure 7 showing the variation of capacitance with frequency at various temperatures

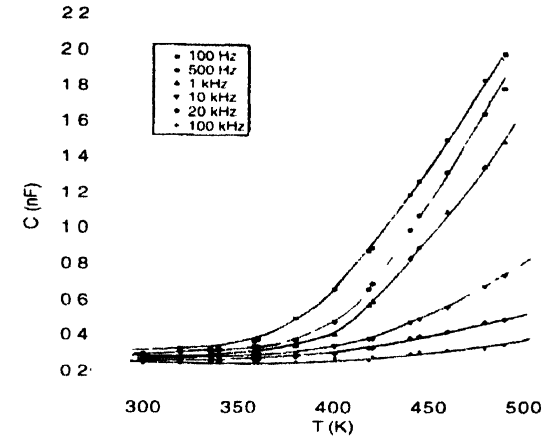

Figure 6. Dependence of the capacitance on temperature at different frequencies

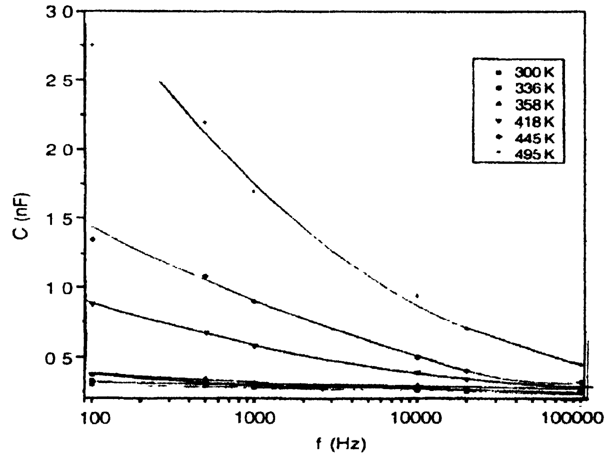

Figure 7. Dependence of the capacitance on frequency at different temperatures.

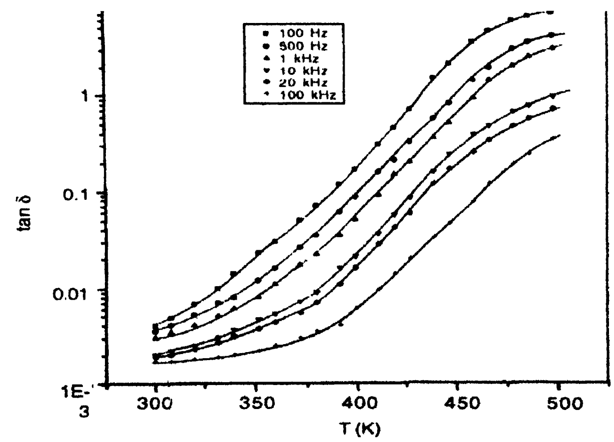

Figure 8. Dependence of the loss tangent on temperature at different frequencies.

(300- 495 K). At temperature of 336K and below, the capacitance is almost frequency, independent but at higher temperatures, the capacitance initially decreases rapidly with increasing frequency and subsequently approaches the low temperature values at higher frequencies. Figures 8 and 9 represent respectively the dependence of tan δ on temperature and frequency ; in all cases, tan δ was found to increase with temperature and to decrease with increasing frequency.

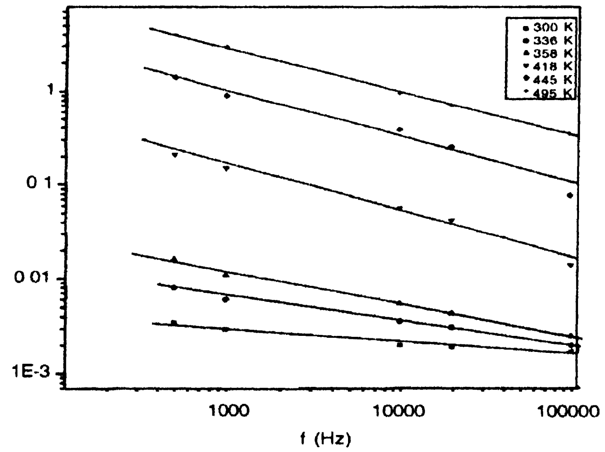

Figure 9. Dependence of the loss tangent on frequency at different temperatures.

4. Discussion

4.1 A.C. Conductivity :

In order to account for the temperature and frequency-dependencies of the a.c. conductivity, various theoretical models have appeared in the literature [10,11]. The a.c. conductivity $\sigma(\omega)$ may often be expressed as a function of frequency according to the following expression [12] :

$$(\sigma) = A\omega^{s} \qquad (1)$$

where ω is the angular frequency, A is a constant independent of frequency [13] and s the frequency exponent.

According to the quantum mechanical tunneling (QMT) model [14], the exponent s is almost equal to 0.8 and increases slightly with increasing temperature or independent on temperature. Therefore, QMT model is considered not applicable to the obtained results.

According to the overlapping – large polaron tunneling (OLPT) model [15], the exponent s is both temperature and frequency dependent, s decreases with increasing temperature from unity at room temperature to a minimum value at a certain temperature, then it increases with increasing temperature. Therefore, OLPT model is also not applicable to the obtained results.

According to correlated barrier hopping (CBH) model, [16] values of the frequency exponent s is ranged from 0.7 to 1 at room temperature and is found to decrease with increasing temperature. This is in good agreement with the obtained results, so the frequency dependence of $\sigma(\omega)$ can be explained in terms of CBH model. The expression for s derived from the basis of this model is given by Elliott [17,18] as

$$s = 1 - \beta = 1 - (6\,kT/W_m), \qquad (2)$$

where W_m is the optical band gap of the material.

According to the Austin-Mott formula [19] based on CBH model, a. c. conductivity $\sigma(\omega)$ can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level.

The dependence of the a.c. conductivity on temperature shown in Figure 4 indicates that the a.c. conductivity is a thermally activated process from different localized states in the band gap [20]. The activation energy of conduction ΔE_σ is calculated at different frequencies from the slopes of lines of Figure 4 using the well known equation

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma / kT), \qquad (3)$$

where σ_0 is the value of σ at $1/T = 0$. The obtained a.c. activation energy at any frequency is much lower than the d.c. activation energy (0.57 ± 0.02 eV) over the same range of temperature. The discrepancy between the d.c. and a.c. activation energies, seems to be obvious since the charge carriers in the d.c. conduction choose the easiest paths which include some large jumps, while this is not so important in the a.c. conduction [21].

It can also be seen that ΔE_σ tends to decrease with increasing frequency as found for semi- conducting materials [22]. The increase of the applied field frequency enhances the electronic jumps between the localized states; consequently the activation energy ΔE_σ decreases with increasing frequency

The discrepancy between the d. c. and a. c. activation energies,the smaller values of the a.c. activation energy and the increase of $\sigma(\omega)$ with the increase of frequency confirm the hopping conduction to be the dominant mechanism.

4.2 Capacitance and loss tangent :

The results shown in Figures 6 - 9 are inconsistent with the model of Simmons *et al* [23] which models the type of thin film structure in terms of a temperature – dependent resistance shunted by a fixed capacitance and in series with two capacitances corresponding to the Schottky barriers existing when using blocking contacts .

This model predicts a maximum in tan δ at a particular frequency (corresponding to a minimum in the quality factor Q)

However, the behaviour obtained from the bulk AgTlSe in the present study may be explained at least qualitatively by the model of Goswami and Goswami [24] originally proposed for ZnS films sandwiched between Al electrodes which act as ohmic contacts for n-type materials. The capacitor system is assumed to comprise a frequency independent - capacitive element C' in parallel with a temperature- dependent resistive element R due to the dielectric material, both in series with a constant low value resistance r.

The measured equivalent series capacitance C_s of the circuit is given by

$$C_s = C' + \frac{1}{\omega^2 R^2 C'} \tag{4}$$

This equation predicts the measured capacitance C_s should decrease with increasing frequency, that C_s decreases with increasing frequency to a constant value C' for all temperatures, and that for any given frequency C_s will increase with temperature because of the decreasing value of R. The loss tangent is given by

$$\tan\delta = \frac{(1 + r/R)}{\omega RC'} + \omega rC' , \tag{5}$$

where ω is the angular frequency. From this equation, at low frequencies, the ω^{-1} term is dominant whereas at higher frequencies, the term in ω is dominant and hence tan δ becomes proportional to frequency and no longer dependent on charge carrier concentrations within the material [25]. Thus, the above equation predicts a decrease in tan δ at low frequency followed by a loss minimum at [15]

$$\omega_m \quad \frac{1}{rRC'^2}^{1/2} \tag{6}$$

and an increase in tan δ at high frequency.

In common with the model of Simmons *et al* [23], the temperature dependence of the characteristics is assumed to be determined through the variation of the interior resistance R *via* a thermal activation process described by

$$R = R_0 \exp\left(-\Delta E/kT\right), \tag{7}$$

where R_0 is a constant. Such behaviour was, for example, observed in various compounds such as thin films of polycrystalline Dy_2O_3 [26] , Cd Te [27] and amorphous SiO - SnO_2 [28]. Similar results have also been obtained in various organic compounds [29-32] . It is clear from the above expressions (4) and (7) that the dependence of capacitance shown in Figures 6 and 7 is broadly as predicted by the model . Furthermore, Figures 8 and 9 show that tan δ also varies with both frequency and temperature as predicted by eqs. (5) and (7).

5. Summary and conclusions

The a.c. conductivity of bulk AgTlSe, seems to be both frequency and temperature-dependent. Regarding the small values of a.c. activation energy , the discrepancy between a.c. and d.c. activation energies and the frequency-dependence of the a.c. conductivity , the conduction mechanism was suggested to be Hopping conduction. In addition, the value of the frequency exponent s and its temperature dependence confirmed the applicability of the CBH model to the investigated bulk AgTlSe.

Both capacitance and loss tangent are found to decrease with increasing frequency and increase with increasing temperature. Such behaviour has been shown to be in qualitative agreement with the model of Goswami and Goswami [24], originally proposed for ZnS films without Schottky barrier. Clearly, although this model predicts the general features shown in our work ,even better agreement would require refinements to the model to include perhaps the effects of the intergranular capacitance in the bulk AgTlSe or the effects of temperature on the series resistance r.

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